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UNITED STATES
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ECONOMIC CONSIDERATIONS IN THE RECOVERY OF MAGNESIA FROM DOLOMITE

BY

ALVIN SCHALLIS

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ECONOMIC CONSIDERATIONS IN THE RECOVERY OF MAGNESIA FROM DOLOMITE[1/]

By Alvin Schallis[2/]

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INTRODUCTION

The problem of supplying enough magnesia for the American war effort has become highly important. Before hostilities began, only about two-thirds of our requirements came from domestic sources; now they must supply almost all the magnesia we need. A further burden is placed upon our own supply by the fact that more and more magnesia is being required, not alone to pace the war tempo of general industrial activity, but also to replace chromite ore in refractories and to make magnesium metal. The domestic magnesite and brucite industry is equipping itself to satisfy much of this greater demand for magnesia, but the remainder must be obtained elsewhere.

The principal sources of magnesia are magnesite, brucite, dolomite or high-magnesium limestone, natural brines, sea water, salt-works bitterns, magnesium silicates, and magnesium salts. Although dolomite is the subject of this paper, it should be considered in perspective with all these highly competitive sources of magnesia.

At present magnesite is the most important source of magnesia. Most of the known commercial deposits of this mineral, however, are far from the principal consuming areas, and the charge for transportation adds considerably to the cost of the magnesia produced therefrom. Several plants are

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being built in Nevada and California to make metallic magnesium. When completed, these may handle as much as half the magnesite produced in the United States, most of the remainder being consumed east of the Mississippi River. The Nevada and California plants utilize the vast reserves of hydroelectric power of that region. Known reserves of high-grade magnesite, however, are not great and at the present rate of consumption will be depleted within a few decades. Utilization of lower-grade magnesite will necessitate employing increasingly expensive beneficiation methods. Despite this, however, magnesite undoubtedly will continue for some time to be the most economical source of magnesia in areas adjacent to its production.

Brucite is another important source of magnesia. The only known domestic deposits of commercial importance are in western Nevada. Conditions with respect to the use of brucite as a source of magnesia are similar to those for magnesite just outlined.

Dolomite is less desirable as a source of magnesia than magnesite or brucite, because the processes for producing magnesia from it are more complex. However its abundance and wide distribution make it the most readily available source in many localities.

Natural brines, sea water, and salt-works bitterns are increasingly important sources and can be used with dolomite as a co-source of magnesia. The synthetic magnesia produced therefrom is cheap and can be strictly controlled as to quality Natural brines and bitterns, however, are not widely distributed throughout the Nation, and supplies are limited. The sea is an unlimited source of supply but is so dilute that recovery of magnesia is difficult.

Magnesium silicates, notably olivine and serpentine, are receiving increasing attention as sources of magnesia. These are abundant in several localities, but recovery of magnesia from them involves chemical processes that have scarcely passed experimental stages.

Magnesium salts, other than those occurring in nature, are not yet employed as sources of magnesia in the United States. In Europe, however, they have been utilized for many years, especially chloride which is a by-product of the potash industry.

Owing to the increasing efficiency of chemical-engineering processes and to the sustained high costs of transportation, a trend toward the use of local sources of magnesia to replace distant sources already has begun. Dolomite which is abundant in the vicinity of many industrial centers, may be treated economically to yield any desired grade of magnesia. It is likely, therefore, that dolomite soon will be one of the more important sources of magnesia

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Some of the various methods by which magnesia or magnesium compounds may be recovered from dolomite as well as their economic possibilities are discussed briefly in this paper. References to patents or to published descriptions of the processes covered in this paper are listed at the end of this paper

RECOVERY OF MAGNESIA FROM DOLOMITE

The various methods proposed for the recovery of magnesia from dolomite fall in two groups - (1) mechanical and (2) chemical. Inasmuch as chemical changes are involved in all processes for separating the constituents of dolomite, mechanical methods are defined as those in which two solids of different properties are separated, and chemical methods as those in which a solid compound of one component is separated from a solution of the other component. Before taking up methods suggested for mechanically separating the lime and magnesia contents of dolomite, it would be well to consider its thermal decomposition.

Thermal Decomposition of Dolomite

Dolomite, $CaMg(CO_3)_2$, is a chemical combination of calcium carbonate ($CaCO_3$) and magnesium carbonate ($MgCO_3$). High-magnesium limestones, mixtures of calcite and dolomite, $CaCO_3 + CaMg(CO_3)_2$ contain higher proportions of calcium carbonate than does true dolomite, but they are commonly called "dolomite" and in this paper are considered as such. Occasionally a mixture (rather than a chemical combination) of calcium carbonate and magnesium carbonate is found which, although having about the same chemical composition, has quite different properties. Such a mixture is often loosely referred to as dolomite, although it may contain none or very little of this mineral. For want of a better name, such material will be referred to in this report as magnesitic limestone. The calcium carbonate and magnesium carbonate constituting this type of material are usually present as particles large enough for successful mechanical separation. Upon heating a magnesitic limestone at atmospheric pressure, the magnesite is decomposed into magnesia and carbon dioxide at its decomposition temperature of 540° C. (1,004° F.) according to values given in the International Critical Tables; but Conley's experiments (1)[3/] seem to indicate that 620° C. would be a more nearly correct value. Calcite does not decompose into lime and carbon dioxide until it reaches about 900° C. (1,650° F.). Although under normal operating conditions the temperature rises much higher than 620° C. before decomposition of the magnesite is complete, it is comparatively easy to decompose the magnesite almost completely and yet allow the calcite to remain unaffected. Such a mixture of magnesia and calcium carbonate is known as differentially calcined or "half-burned" dolomite.

3/ See references at the end of this report.

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Magnestic limestones are not readily overcalcined. Calcination at a temperature just high enough to drive the carbon dioxide from the calcium carbonate gives a material in which both the magnesia and lime are extremely reactive. Increasing the temperature well above this level decreases the reactivity of the magnesia but affects the lime but little.

True dolomite, however, reacts very differently. At atmospheric pressure it begins to decompose at about 725° C. (1,337° F.), according to Conley (1). At this temperature, in the absence of suitable catalysts, the double carbonate breaks down yielding calcite and magnesite. The latter, being above its decomposition temperature, immediately decomposes into MgO and CO_2. Although the calcite formed by the decomposition of true dolomite does not evolve CO_2 below the usual temperature of about 900° C. (1,650° F.), it will be noted that the spread between the temperature of decomposition of the magnesite and that of the calcite is considerably less for true dolomite than for magnesitic limestone. It follows that true dolomite is more difficult to calcine differentially or to "half burn" than such a mixture.

Again, in contrast to the mixture of calcium and magnesium carbonates, true dolomite may readily be overcalcined. Owing to the intimacy of contact between the magnesia and the lime, calcination at too high a temperature or for too long a period is very likely to reduce substantially the reactivity not only of the magnesia but of the lime as well. Certain impurities, especially iron or aluminum oxides, aggravate this tendency and increase the care with which the dolomite must be calcined to avoid overburning.

Production of "Half-Burned" Dolomite

Inasmuch as the half burning of dolomite is a prerequisite of several processes discussed in this paper, and because the magnesia in half-burned dolomite finds important uses in the manufacture of magnesium oxychloride cements, fertilizers, and for water softening, a brief discussion of methods of half burning dolomite is desirable.

Owing to the narrow temperature range for calcining dolomite differentially, attempts to use the usual calcining methods or apparatus invariably result in either the incomplete calcination of the magnesium carbonate or the formation of free lime. For some uses, free lime is so objectionable that no more than traces of it may be tolerated; but, on the other hand, incompletely calcined magnesium carbonate results in loss of yield. To overcome these difficulties, numerous studies have been made and many methods of calcining devised to "half-burn" completely dolomite so as to produce magnesia containing no more than traces of free lime.

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Loomis (2) suggests that large lumps of dolomite be half-burned by calcining in an ordinary lime kiln operated at a temperature somewhat lower than usual. The calcined lumps are then treated with enough water to slake only the material on the outer surface that is high in free lime. This causes the surface material to crumble and leave a core relatively free of calcium oxide. Although in this method slight overburning to assure complete calcination of the dolomite is not objectionable, the temperature must be kept low enough to confine the CaO to a thin surface layer. To broaden the spread between the temperature at which MgO is formed and the temperature at which CaO is formed from true dolomite, the partial pressure of CO_2 in the atmosphere surrounding the dolomite should be increased, because such increase will raise the temperature of decomposition of $CaCO_3$ but will have no effect upon the decomposition of dolomite into magnesite and calcite (3). As it is the difference between these two temperatures that permits differential calcination of dolomite, it follows that an increase in the partial pressure of CO_2 above the dolomite will facilitate the differential calcination of dolomite to MgO and $CaCO_3$.

McIntire (4) suggests the use of 100-mesh material agitated at 500° to 550° C. in a current of steam to maintain a low partial pressure of CO_2. The steam also acts catalytically on the double carbonate to hasten its decomposition into calcite and magnesite and thus to increase greatly the range of temperature for differential calcination. The fine particle size of the dolomite is essential because the steam can penetrate only as far as decomposition of $MgCO_3$ has left the dolomite porous. Decomposition involves expulsion of CO_2 and its diffusion through the layers of porous reaction product to the surface of the particle. Inasmuch as the direction of this diffusion is opposite that of the diffusion of water vapor the rate of reversion and decomposition of the dolomite will decline rapidly as the layer of reaction products becomes thick; but when the rock is in small particles, the layers are always thin. The use of finely divided material is contrary to normal practice, because relatively coarse material has more desirable physical characteristics. Large quantities of finely divided dolomite are available, however, as byproducts of various other mineral industries, including tailings from ore-concentrating mills using froth flotation.

Stump (5) has described a process of carbonating the $Ca(OH)_2$ content of a milk of dolomitic lime to produce a suspension of $CaCO_3$ and $Mg(OH)_2$. Pike (6) describes a somewhat similar process whereby freshly calcined dolomite is subjected to the action of CO_2 and H_2O in a closed vessel at 300° to 600° C. until all the CaO is converted into $CaCO_3$, thereby producing a fairly high-grade half-burned material. The processes of Stump and Pike, or modifications of them, could no doubt be employed advantageously to eliminate any free lime inadvertently formed in half-burned dolomites.

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Methods of Mechanical Separation of Lime and Magnesia in Dolomite and Magnesitic Limestone

Methods dependent on differential calcination and hydration. - Of the various mechanical methods of obtaining magnesia from magnesitic limestone, perhaps the simplest is to "half burn" the material, producing a friable MgO, whereas the calcite remains unchanged. The magnesia is then easily disintegrated and separated by screening. This process has been described by Mitchell and others (7). Although it would be virtually impossible to obtain a complete separation because some of the calcite would be reduced to a fine state during crushing and some of the magnesia would not be reduced, the method would probably be suitable and economical for the manufacture of stabilized dolomitic refractories. Obviously, the method applies only to magnesitic limestones.

An improvement over the above method consists in slaking the caustic magnesia with barely enough water and carbon dioxide to convert it into a fine, light, fluffy, basic magnesium carbonate powder. This puts no mechanical stresses on the calcite, and as only a small part of it is reduced to the fineness of the magnesia, satisfactory separation may be obtained either by screens or by air classifiers (8). The basic magnesium carbonate so produced is light enough to be used directly in thermal insulation, or it may be converted into clacined magnesia products. This method is very simple, but any calcium oxide formed in the half-burned magnesitic limestone would contaminate the product. Considerable care must therefore be taken in the preparation of a half-burned magnesitic limestone that is virtually free of calcium oxide.

Somewhat similar are the processes of Clerc, Nihoul, and others (9), in which magnesitic limestone is calcined at 1,000° to 1,200° C. to produce a relatively hard-burned dolomite. This product is treated with only enough water to hydrate the lime but not enough to hydrate the magnesia. In this instance the calcium hydroxide takes the form of a fine powder that may be separated from the coarser MgO by screening. Obviously, this process would not be effective for true dolomite, as both the MgO and the CaO resulting from calcining would be very fine-grained, with no appreciable difference in particle size. Its basic principle is the comparative ease with which MgO may be rendered inert to water and CO_2 by means of heat treatment.

Goudge (10) employed a modification of the Clerc and Nihoul process to recover a relatively pure magnesia from brucitic-limestone deposits of Ontario and Quebec, Canada. This material, similar in many respects to magnesitic limestone, consists of roughly spherical granules of brucite commonly 1 to 4 mm in diameter embedded in a matrix of limestone. Occasionally, dolomite and granules of serpentine are found associated with the brucitic limestone. In general, the granules of serpentine are smaller than those of brucite.

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In Goudge's process, uniformly graded brucitic limestone is calcined at 1,000° to 1,200° C. depending on the presence of dolomite in the material. Owing to the comparative ease with which dolomite may be overburned, it is necessary to treat the brucitic limestone containing dolomite at a temperature not higher than 1,000° C. Inasmuch as brucite ($Mg(OH)_2$) decomposes with the evolution of water at 700° to 900° C., such treatment leaves this material as relatively inactive magnesia.

The next step in the process is to slake the lime or calcined dolomite with just enough water to produce a dry hydrate. To facilitate the penetration of water, it is desirable to crush the calcine to finer than 3/4-inch size. It is necessary to prevent the temperature in the slaking mass from rising unduly, inasmuch as this facilitates hydration and consequent loss of the calcined brucite granules. With properly calcined material, a carefully controlled slaking operation should yield a satisfactorily differentially hydrated product.

Separation of the inactive magnesia granules from the fine, hydrated lime is accomplished by air separation, and the magnesia granules are discharged to a washing unit for removal of adhering lime dust and hydration of any unslaked lumps of lime that may remain after the primary slaking operation. The hydrated lime thus separated may be marketed economically in many localities. The granules are collected on either a 35- or a 65-mesh screen, depending on the presence of serpentine grains and the purity of product desired. The serpentine grains derived from brucite, being finer for the most part than the magnesia grains, usually pass a 35-mesh sieve and thereby leave a relatively pure magnesia product.

By this process Goudge has been able consistently to recover magnesia of 90 to 94 percent MgO in yields of 15 to 18 percent from rock containing 28 to 32 percent MgO. Actually, the recovery of magnesia granules is somewhat higher than is indicated by the above figures, inasmuch as appreciable quantities of the MgO in the original rock are present as dolomite. A plant using this process is now in operation at Wakefield, Quebec.

The Kilbourn process (11) likewise depends on the fact that lime hydrates more rapidly than magnesia. Instead of using a dry particle-separation process, however, Kilbourn removed the lime by elutriation, leaving a coarse product high in magnesia. This process eliminates the precise control of water and temperature involved in the dry process. The resulting wet magnesia must be dried, but drying may present no real problem because the product would be used chiefly for refractories that must be calcined, and the presence of moisture might even facilitate mixing of various conditioning and stabilizing agents.

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Other methods. - According to a method proposed by Auzies and Segoffin (12), the dolomite or magnesitic limestone is calcined at 900° to 950° C., and the product is completely slaked to $Mg(OH)_2$ and $Ca(OH)_2$. The $Ca(OH)_2$ normally precipitates in relatively coarse grains, and coarse crystallization is facilitated by employing a highly concentrated slurry. Concentrations as high as 3.7 pounds of MgO + CaO per gallon of slurry have been suggested. The $Mg(OH)_2$, however, precipitates in a fine colloidal state, and this difference in grain size permits a fair separation by elutriation. Magnesia concentrations as high as 80 percent may be obtained by this method. Obviously, this process is applicable to both magnesitic limestones and true dolomites.

Stump (5) has developed a method for the carbonation of the $Ca(OH)_2$ to aid in the separation of calcium from the magnesium components. The precipitation must be carried out carefully so that the calcium carbonate may be settled readily and not interfere with the $Mg(OH)_2$ that remains as a relatively stable colloidal suspension.

The separation of magnesia from dolomite by flotation was studied by Stull (13) and du Bois (14). Stull boiled calcined dolomitic material in water, and a product containing 65 to 75 percent magnesia was obtained by froth flotation. In the method of du Bois, dolomite is halfburned, finely ground, and is added to an emulsion of a hydrocarbon or other oil in water. The calcined dolomite decomposes into $CaCO_3$ and $Mg(OH)_2$. The $CaCO_3$ is froth-floated by means of compressed air, and the $Mg(OH)_2$ remains in suspension in the liquid and is recovered subsequently by filtration or by various settling and thickening devices. These flotation processes appear to be applicable to both true dolomites and magnesium limestones.

Stull (13) suggested that just enough H_2SO_4 be added to calcined dolomite (probably milk of dolomitic lime) to convert the calcium hydroxide into calcium sulfate, which forms in relatively large needle-shaped crystals. These crystals are then readily separated from the finer $Mg(OH)_2$ by a screening or other size-classifying operation. A product containing 75 percent MgO has been obtained by this method.

Stull's method has the disadvantages that the product is rather low in MgO and it employs an expensive raw material, sulfuric acid. Nevertheless, it might be used for dolomite in conjunction with brines containing magnesium sulfate, as suggested by Scheibler (13), or heavy metal sulfates - whether natural brines or industrial waste products. Inasmuch as rather complicated chemical reactions are involved in the use of these solutions, the processes will be discussed in more detail in another section of this paper.

As the mechanical separations of the lime and magnesia content of dolomite or magnesitic limestone are all relatively simple and are not

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dependent on other manufacturing operations or byproducts, they may be conducted at points convenient to sources of dolomite and markets for the products. For the most part, the processes are inexpensive to operate and require little or no raw material other than dolomite, water, and sources of energy, such as coal or other fuel. Moreover, they are all well adapted to large-scale operations and require but simple equipment. However, magnesitic limestones are far from abundant, and the relatively impure products obtained from true dolomite by these mechanical methods compete unfavorably with the more highly concentrated products now on the market. For these reasons, no large-scale recovery of magnesia from either dolomite or magnesitic limestone by purely mechanical means is accomplished in the United States at the present time.

Processes for Chemical Separation of Lime and Magnesia in Dolomite

1. Solution of calcium hydroxide in water.

The components of a mixture of two substances may readily be separated, no matter how intimately they may be mixed, if one of them can be rendered soluble in a fluid in which the other is relatively insoluble. Numerous methods for accomplishing this end with respect to dolomite have been devised. Perhaps the simplest of these is based upon the differential solubility of calcium and magnesium hydroxides in water. The solubility of $Ca(OH)_2$ in water at 18° C. is 1.63 gm. per liter, whereas that of $Mg(OH)_2$ is only about 0.009 gm. per liter (15). These figures reveal the possibility of dissolving the $Ca(OH)_2$ from calcined and slaked dolomite without appreciable loss of $Mg(OH)_2$. This principle has long been recognized, but until recently the many attempts to employ it have failed to develop a commercially successful process.

Handy and Isham (16) describe a process in which lightly calcined dolomite (calcined at 900° to 950° C. to remove all the CO_2 without dead-burning the lime) is granulated to the size of a pea and is leached with cold water to produce an MgO product containing 3 to 10 percent CaO. The calcining operation must be conducted carefully if maximum purity is to be attained. Too low a temperature will give incompletely calcined material with quantities of insoluble $CaCO_3$ remaining. Too high a temperature may cause the dolomite to become difficult to hydrate and may also cause the formation of insoluble and slowly soluble calcium compounds such as silicates which also contaminate the product.

Eyoub (17) agitated various calcined dolomites in water for 10- minute intervals, allowed the insoluble material to settle, siphoned off the supernatant liquor, and washed the residue with fresh water. The insoluble

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residues, after drying and calcining, averaged: Magnesia, 81.2 percent; lime, 4.1 percent; insoluble, 13.9 percent. Some of the products thus obtained were suitable for the manufacture of magnesium oxychloride cement, and all were satisfactory for refractory purposes.

Stull (13) and Frankel (18) obtained unsatisfactory results with this process, the low magnesia content of their products probably being due to improper calcining and the use of water containing small quantities of CO_2.

In 1939 the Standard Lime & Stone Co. of Baltimore, Md., began the commercial production of a high-magnesia basic refractory material from dolomite by a process of leaching the lime from the calcined dolomite with water. This process is covered by patents issued to Young and Triggs (19) and may be described briefly as follows: Dolomite is calcined to produce a soft-burned CaO component (between 900° and 950° C.), and the calcined material is slaked while still hot with enough CO_2-free water at a temperature above 50° C. to produce a milk of lime. This is next treated in a bowl classifier to remove large or heavy aggregates of unburned lime, silica, or silicates, and then agitated to disperse the particles of $Ca(OH)_2$ and $Mg(OH)_2$. Enough CO_2-free water is added to dissolve the $Ca(OH)_2$ (about a thousand parts of water per part of lime). The diluted milk of lime, violently agitated to facilitate the dissolution of the $Ca(OH)_2$, is run into a Dorr thickener; the product is a sludge of $Mg(OH)_2$ containing about 9 percent CaO and 1 percent other impurities on a dry basis. The sludge is further dewatered on an Oliver continous rotary filter. After additions of iron oxide and silica as fluxes, the filter cake is calcined in a rotary kiln to produce a refractory-grade magnesia.

The clear overflow from the Dorr thickener is treated with enough CO_2 from the dolomite-calcining operation to precipitate most of the $Ca(OH)_2$ as $CaCO_3$, but not enough to leave any residual CO_2 in the purified solution. The suspension of $CaCO_3$ is settled in a Dorr thickener, and the water is re-used. The precipitated calcium carbonate, although of good quality, is unused.

This process is economical because it is simple, requires no chemical reagents and operates independently of other processes or products. Enormous quantities of water must be handled, however, and the apparatus required must therefore be correspondingly large. This entails a large capital outlay in plant equipment, but operating costs are relatively low, inasmuch as pumping against low heads, settling, and thickening are among the least expensive of chemical-engineering operations. As final filtration is conducted on moderately concentrated slurries, its cost is not excessive.

A serious objection to the process is the high lime content of the product. Purity of the magnesia could be increased by adjusting the process, but the

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rate of the production would be decreased. It is claimed that the lime content cannot economically be reduced below 2 percent, and that to maintain low operating costs a considerably higher content must be allowed. The high lime content limits the usefulness of the product but does not prevent its employment for the major use, namely, the preparation of dead-burned grain magnesia for lining open-hearth furnaces.

Impure magnesia may result from reasons other than incomplete leaching of the lime: (1) Undecomposed calcium carbonate may be present; (2) silica, alumina, iron oxide, or other insoluble impurities will remain with the magnesia; (3) acidic oxides may react with the lime to form insoluble compounds during calcination; (4) insoluble compounds may so enclose quantities of lime as to prevent dissolution; or (5) some of the lime may be overburned and thus rendered difficultly soluble. These factors apply to any operation that leaches out the lime as a soluble calcium salt and leaves the $Mg(OH)_2$ as an insoluble residue. Inasmuch as dolomite usually contains only about 20 percent MgO, impurities in the raw dolomite increase fivefold in percentage when they remain with the magnesia. For these reasons, the use of high-grade dolomite and careful purification of milk of dolomite are essential to the production of a satisfactory magnesia product by a lime-leaching process.

2. Processes Involving Use of Sugar.

Many attempts have been made to facilitate the leaching process by adding solutes to increase the solubility of $Ca(OH)_2$ in water. Sugar is one of the few solutes on which a commercially successful process is based. Bernard and Ehrmann (20) have described such a process.

The reactions are as follows: When $Ca(OH)_2$ is added to a solution of sugar (sucrose), soluble calcium sucrates are formed until about 2 mols of $Ca(OH)_2$ is added for each mol of sugar present in solution. Further addition of calcium in the form of dry, powdered CaO to a solution cooled to below 10°C. causes the formation of an insoluble compound that corresponds to the formula $C_{12}O_{11}H_{22} \cdot 3CaO \cdot XH_2O$. This insoluble calcium sucrate may be redissolved by the addition of more sugar to the solution. Several known sucrates are formed during these reactions, some of which are listed below:

Calcium monosucrate	$C_{12}O_{11}H_{22} \cdot CaO$
Sesqui calcium sucrate	$(C_{12}O_{11}H_{22})_2(CaO)_3$
Dicalcium sucrate	$C_{12}H_{22}O_{11} \cdot 2CaO$
Tricalcium sucrate	$C_{12}H_{22}O_{11} \cdot 3CaO$

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The solubility of $Ca(OH)_2$ in aqueous sugar solutions at 25° C. is indicated in the following table 1/:

Solubility of calcium hydrate in sugar solutions of varying concentrations

$Ca(OH)_2$ dissolved, percent	Sugar in solution, percent	Water, percent	Specific gravity
0.117	0.00	99.88	0.983
.188	.62	99.19	1.000
.730	4.82	94.50	1.021
1.355	7.50	91.12	1.037
2.31	9.87	87.85	1.051
3.21	11.90	84.89	1.067
4.57	15.10	80.33	1.092
5.38	17.42	76.93	1.109
6.07	19.86	73.07	1.123

Scheibler (21) obtained patents on a somewhat similar process that now bears his name. According to this process, a heavy milk of dolomite is treated with an excess of 10 percent molasses solution. The $Ca(OH)_2$ goes into solution as a sucrate, and the magnesia remains unaffected. The magnesium hydroxide is filtered from the viscous calcium sucrate solution, washed, and calcined to magnesia. The calcium sucrate solution is treated with CO_2 from the dolomite-calcining operation to precipitate $CaCO_3$ and to regenerate the sugar solution. A typical analysis of the magnesia obtained in a German plant using this process is given by Eckel (22), as follows:

	Percent
MgO	95.99
CaO	2.18
SiO_2 -- Al_2O_3 -- Fe_2O_3	1.47

Considerable work has been done on this process, and many modifications have been suggested. Pauling (23) recommends that the reactions be carried out at 20° to 30° C. to produce easily settleable and filterable $Mg(OH)_2$ and $CaCO_3$ deposits, whereas Frankel (18) claims that as the formation of $CaCO_3$ from calcium sucrate solution is slow and the precipitate is almost colloidal, the reaction between CO_2 and calcium sucrate should be carried out at or near the boiling point of the solution to facilitate precipitation by the formation of larger particles. Frankel found that solutions containing 10 to 15 percent of sugar were most effective because more concentrated solutions were too syrupy and prevented complete solution of the $Ca(OH)_2$. Moreover, concentrated solutions tended to cause the magnesium hydroxide to

1/ Cameron and Patten: Jour. Phys. Chem., vol. 15, 1911, p. 70.

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"lump" and coagulate rather than remain as a fine sludge. To avoid the formation of the insoluble tricalcium sucrate, an excess of sugar over the theoretical requirements is necessary if the calcined dolomite is added to the sugar solution before hydrating. Nees (24), however, claims that $Ca(OH)_2$ does not cause the formation of insoluble tricalcium sucrate.

The Scheibler process has an advantage over simple leaching of the $Ca(OH)_2$ from milk of dolomite with water in that considerably smaller volumes of solution must be handled, but sugar losses are relatively high. About 11 gallons of 10 percent molasses solution are required per pound of magnesia produced, and almost 5 percent of the sugar content of this solution is lost in each cycle. Part of this loss is through handling of the material and part is due to adsorption on the calcium carbonate precipitate. Frankel (18) found that the precipitated $CaCO_3$ contained 7 to 8 percent sugar, and that incomplete carbonation does not break up the sucrocarbonates, which are stable until an excess of CO_2 is passed through the solution. Such a reagent loss adds considerably to the cost of production and thereby greatly reduces the advantage of reduced volumes of solution to be handled. Another objection to the Scheibler process is that the separation of the magnesium hydroxide and the calcium carbonate from their respective mother liquors is rendered difficult by the viscosity of the solutions.

The Scheibler process demands a source of very cheap sugar solutions and, with modifications, could be included in the sugar-refining process, magnesia being obtained as a byproduct (25). Such a process is now used in some European plants (26). High-magnesium lime is used and the undissolved magnesium hydroxide is separated from the solution before calcium carbonate is precipitated. The magnesium hydroxide is an active adsorbant of impurities in the sugar solution, but the impurities are largely organic and are therefore removed by subsequent calcination.

The Steffen is another sugar-refining process in which magnesia may be produced as a byproduct. In this process, dry, powdered lime is added to relatively dilute cold syrups (usually beet) to produce insoluble tricalcium sucrate and leave an almost sugar-free solution. The process may be modified (27) by adding milk of high-magnesium lime to the dilute syrup to the extent of the solubility of the lime, after which tricalcium sucrate is precipitated by adding dry, powdered high-calcium lime or high-magnesium lime. The suspension of mixed $Mg(OH)_2$ and tricalcium sucrate is removed by filtration, washed, and treated with enough warm sugar solution to dissolve all the tricalcium sucrate and any calcium hydroxide that may have formed during the precipitation. The $Mg(OH)_2$ is separated from the lime-sugar solution and is calcined to produce magnesia for refractory, oxychloride cement or other purposes.

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Because of the enormous size of the sugar industry, these byproduct processes offer a huge potential source of magnesia. Some losses of sugar not ordinarily experienced in the usual sugar-refining process will occur during the manufacture of magnesia by these processes, and this will reduce the margin of profit in the operation. Moreover, the nature of the magnesia is so far removed from the nature of sugar, and the margin of possible profit is comparatively so low, that the production of magnesia as a byproduct has not appeared attractive to most of the domestic manufacturers of sugar. Nevertheless, magnesia is being produced by these methods in Europe, and serious consideration is being given to it in the United States.

3. Processes Involving Use of Hydrogen Sulfide or Sulfur.

Another means of obtaining magnesia from dolomite, which has been the subject of considerable study, is the process or series of processes involving hydrogen sulfide. The most direct of these methods is that recently studied on a pilot-plant basis by the Warner Co. of Philadelphia, Pa., and for which a large commercial plant is now being constructed. In this process, H_2S is passed into a purified milk of dolomitic lime forming a solution of calcium bisulfide ($Ca(HS)_2$) but leaving the $Mg(OH)_2$ unaffected. The latter is recovered by filtration or settling and the solution of $Ca(HS)_2$ is treated with CO_2 to release the H_2S for re-use and to precipitate $CaCO_3$. The $Mg(OH)_2$, which contains all the silica and iron present in the original suspension, is calcined to commercial grades of MgO. Some degree of control is necessary in the operation of this process to assure complete reaction of the $Ca(OH)_2$ without the formation of appreciable quantities of $Mg(SH)_2$.

MacIntire (28) described a process in which half-burned dolomite is ground with water and enough CO_2 is passed into the slurry to recarbonate any free lime without affecting the $Mg(OH)_2$ appreciably. After all of the $Ca(OH)_2$ is reacted, H_2S is passed into the suspension to form a solution of $Mg(HS)_2$. The $CaCO_3$ is filtered from the $Mg(HS)_2$ solution, and the latter is boiled to precipitate $Mg(OH)_2$ and to release the H_2S for further use. Under carefully controlled conditions, the $Mg(OH)_2$ produced may be very pure, inasmuch as impurities in the dolomite remain largely with the precipitated $CaCO_3$. By imperfect operation, however, some calcium hydroxide may remain to contaminate the product. Moreover, if handling and boiling of the bisulfide liquor are not carefully controlled, sulfur compounds may remain in the final product. However, the processes are inherently simple and offer the possibility of yielding products of high purity, which may be manufactured under closely controlled conditions. Processes for the separation of magnesia from dolomite with the aid of hydrogen sulfide are of interest also because of the comparatively large sources of byproduct or waste hydrogen sulfide in the petroleum industry, manufacture of sulfur dyes, purification of fuel gas for domestic consumption, and in many other industries.

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Drewsen (29) patented a process for the production of magnesia and calcium pentasulfide by treatment of milk of dolomitic lime with sulfur which reacts with the calcium hydroxide at the boiling point of water to form calcium polysulfide and calcium thiosulfate, but does not react with the magnesia. Unfortunately, the calcium thiosulfate so formed is unstable under the usual conditions of the reaction and breaks down into the insoluble calcium sulfite and sulfur. The precipitated sulfur may react with additional calcium hydroxide, but the calcium sulfite remains with the magnesia as an insoluble residue. The net reaction is as follows:

$$\underbrace{3Mg(OH)_2 + 3Ca(OH)_2}_{\text{Milk of dolomitic lime}} + 11\ S \dashrightarrow \underbrace{2CaS_5 + 3H_2O}_{\text{Solution}} + \underbrace{3Mg(OH)_2 + CaSO_3}_{\text{Insoluble residue}}$$

The insoluble residue, consisting of $Mg(OH)_2$ and $CaSO_3$ is removed by filtration and calcined to remove SO_2. The resulting product theoretically contains 68 percent MgO and 32 percent CaO. It is possible that a satisfactory basic refractory material may be produced from this material if, before calcining, enough silica, preferably in the form of magnesium silicates, is added to react with the CaO and form calcium orthosilicate. Suitable quantities of a stabilizing agent for the calcium orthosilicate, such as iron oxide or chrome ore, should also be added and the mixture calcined at a suitable temperature. The insoluble residue from the lime-sulfur reaction may also be used directly as a fertilizer ingredient without calcining. This use requires only that the product be satisfactorily dried and ground. Both components of the product would be utilized, the $Mg(OH)_2$ acting as a conditioning and neutralizing agent and the $CaSO_3$ acting to furnish sulfur and lime to the soil.

This process could be modified by employing enough H_2S to form calcium sulfide and eliminate the formation of calcium sulfite; the insoluble residue obtained thereby would contain no calcium or sulfur compounds other than those insoluble compounds in the original dolomite and possibly small quantities of impurities formed by side reactions during the process. The yield of calcium pentasulfide obtained from a given sulfur input would likewise be improved.

Considerable quantities of calcium polysulfide are produced each year for fungicidal purposes, thus making this industry a potential source of magnesia of some importance. The type of concern that manufactures calcium polysulfide could no doubt best capitalize upon the fertilizer-ingredient use for the magnesia-calcium sulfite product of the reaction, although a product entirely free of calcium compounds as produced by the H_2S reaction could

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doubtless also find a market. The lime-sulfur industry however, is, seasonal, therefore, it could not satisfactorily produce magnesia other than for fertilizers, the markets for which are also seasonal.

4. Processes Involving Use of "Solution Aids".

In addition to the uses of sugar and H_2S, other attempts have been made to facilitate the solution of $Ca(OH)_2$ in leaching the lime from calcined dolomite. Several of these that involve "solution aids" (reagents that increase the solubility without themselves being consumed) probably will not become important commercially because of their slight advantages or high cost. They are discussed here because of their possible application as byproducts.

The solubility of $Ca(OH)_2$ is increased by the presence of various solutes in solution, especially calcium salts. The following table indicates this effect by giving data from the observations of various workers on a few salt solutions.

$Ca(NO_3)_2$ at 100° C. is the most effective of the salts shown in increasing the solubility of $Ca(OH)_2$, but it probably will not be used commercially in the separation of lime and magnesia from dolomite, because its effect is much less than that of the sugar solution, its concentration must be very carefully controlled at 57.0 percent $Ca(NO_3)_2$ for optimum results, and its cost is about $23 per ton of $Ca(NO_3)_2 \cdot 4H_2O$.

Gathy, and later Esch (30), recommended the use of $CaCl_2$ solution to leach lime from calcined dolomite because at high temperatures it will dissolve several times as much $Ca(OH)_2$ as would be dissolved in water. The use of the $CaCl_2$ solution would reduce the size of the apparatus necessary for a given capacity or increase the capacity of a given unit, and may prove economical inasmuch as large volumes of impure $CaCl_2$ solutions are obtained as waste in the Solvay process for production of sodium carbonate. In a Solvay process plant, it would seem more economical, however, to separate the lime and magnesia directly in the process itself, as will be discussed later, rather than as a separate step. There are, moreover, cyclic processes involving $CaCl_2$ that operate satisfactorily and yield considerably higher solution and suspension concentration of the active materials involved. However, as these processes are somewhat more complicated to operate, close study would be necessary to determine the most satisfactory procedure.

Solubility of $Ca(OH)_2$ in water is somewhat increased by the presence of salt. This effect is slight but may be used to advantage in areas in which natural brines or salt deposits are available. Possibly even sea water may be employed to advantage in processes involving the water-leaching of lime from dolomite, although here, again, other processes appear to be more attractive.

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Solubility of $Ca(OH)_2$ in solutions of various electrolytes

Concentration of solubilizing electrolyte, percent	Solubility of $Ca(OH)_2$ in indicated solutions, expressed in percentage of solution				
	$Ca(NO_3)_2$ 1/		$CaCl_2$ 2/		NaCl 3/
	25° C.	100° C.	20° C.	100° C.	Room temperature
0	0.153	0.065	0.125	0.090	0.18
5	.14	.08	.137	.091	.235
10	.145	.11	.168	.139	.24
15	.16	.14	.199	.184	.20
20	.18	.185	.186	.233	.16
25	.20	.24	.166	.371	.12
30	.23	.31	.163	.492	---
35	.275	.40	4/.156	---	---
40	.335	.54	4/.054	---	---
45	.38	.79	4/.000	---	---
50	.26	1.20	---	---	---
55	.20	1.86	---	---	---
60	.00	1.87	---	---	---
65	---	1.465	---	---	---
70	---	1.57	---	---	---
75	---	1.15	---	---	---
80	---	.00	---	---	---
Maxima	0.41 at 44.4	2.25 at 57.0 1.67 at 70.6	0.215 at 17 4/0.254 at 33.7	---	0.245 at 7.5

1/ Bassett and Taylor: Jour. Chem. Soc., vol. 105, 1914, p. 1926.
2/ Zahorsky: Zeit. anorg. Chem., vol. 3, p. 34.
3/ Maigrit: Bull. Soc. Chim. Paris, vol. 33, No. 3, 1905, p. 631.
4/ Schreinemakers and Figu: Chem. Weekbl., vol. 8, 1911, p. 685. (Data are for a temperature of 25° C.)

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Calcium hydroxide is appreciably soluble in cool ammonium chloride solution or in other ammonium-salt solutions. (It is likewise soluble in solutions of the salts of any weak base.) This is principally because of the formation of the corresponding calcium salt and ammonium hydroxide, which remain in solution at low temperatures. Proposed processes based on this fact will be considered in a subsequent section of this paper.

The separation of calcium hydroxide from milk of dolomitic lime by reaction with phenol or one of its homologues to form a soluble calcium salt has been suggested (31). The insoluble $Mg(OH)_2$ is removed, after which the phenolic reagent and calcium carbonate are recovered by treatment of the calcium salt with CO_2. Numerous solvents other than water may be used in this process; among the more common are alcohol or acetone. Because of the relatively high cost of the reagents, however, it is probable that this process would be uneconomical except as a byproduct activity.

A disadvantage common to all processes that employ appreciable concentrations of soluble salts is the difficulty of washing the magnesia free of the soluble salts, because magnesia is a troublesome product to handle.

5. Magnesium Bicarbonate Processes.

Findeisen (32) and Pattinson (33) devised, perhaps, the earliest processes for the separation of lime and magnesia from dolomite by fractional solution with carbonic acid. Pattinson's process and modifications thereof have since become widely employed in the manufacture of the comparatively high-cost product, basic magnesium carbonate.

In the Pattinson process dolomite is calcined and slaked to form a milk of dolomite, which is then classified to remove impurities and is treated with washed and compressed kiln gases to produce precipitated $CaCO_3$ and form $Mg(HCO_3)_2$ in solution. The $CaCO_3$ is filtered off, dried, and marketed as precipitated calcium carbonate whiting, agricultural lime, or for pharmaceutical purposes, cements, paints, and other products. The clear $Mg(HCO_3)_2$ solution is boiled for a short time to precipitate basic magnesium carbonate from solution and liberate CO_2 in a relatively pure state. The carbon dioxide, because of its purity, is either returned to the process or is compressed and marketed. The precipitated basic magnesium carbonate is separated from the relatively pure water by filtration and is carefully dried. The water is returned to the process for producing more milk of lime. The basic carbonate has a low specific gravity and is used in "85-percent magnesia" heat insulation or in the manufacture of pharmaceutical goods, face powder, toilet articles, rubber goods, or other products. Some of the basic carbonate is calcined to produce "light burnt calcine (pure MgO)" for the pharmaceutical, chemical, and rubber trades.

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Many modifications of this basic process have been suggested. Lemoine (34) found that by digesting finely divided dolomite with water charged with CO_2, the $MgCO_3$ dissolves more rapidly than the $CaCO_3$. It should therefore be possible to separate the $MgCO_3$ from the $CaCO_3$ in dolomite without the necessity of previously calcining the material, but in actual practice it is so much easier to bring the magnesia of calcined dolomite into solution as the bicarbonate than to dissolve the magnesia of raw dolomite with carbonic acid that the additional cost of calcination is justified. Magnesium carbonate precipitated from the hydroxide by addition of CO_2 is crystallized with three molecules of water to form $MgCO_3 \cdot 3H_2O$, which is 8.7 times as soluble as $MgCO_3$ and considerably more reactive.

Henton and others (35) suggested that the dolomite be only "half burnt" to facilitate calcination and to make use of the enhanced reactivity of the precipitated magnesium carbonate while the $CaCO_3$ content remains inactive.

It is customary to carbonate the milk of dolomitic lime at moderate pressures above atmospheric, although Henton (35) found that an equal reaction occured when kiln gases were used at atmospheric pressure. He attributed the ineffectiveness of increased pressure to the formation of protective films of inert gases about the particles. The relationship between the partial pressure of CO_2 over a solution and the solubility of $MgCO_3$ in the solution is shown in the following table.

Relationship between the solubilities at room temperature of $MgCO_3$ and of $CaCO_3$ in water containing CO_2 and the partial pressure of CO_2 above the solution.

Pressure of CO_2 atms.	$MgCO_3$ per liter, gm.	$CaCO_3$ per liter, gm.	Ratio $MgCO_3$; $CaCO_3$, gm.
0.0	0.92	0.015	61.0
1.0	27.8	.94	29.5
2.0	32.7	1.19	27.5
3.0	37.2	1.37	27.1
4.0	41.3	1.54	26.8
5.0	44.5	1.70	26.2
6.0	47.8	1.84	26.0
7.0	50.9	1.96	26.0
8.0	53.5	2.08	25.8

The data for magnesium carbonate in the above table were taken from Engel and Ville (Compt. rend., vol. 93, 1881, p. 340, and those for $CaCO_3$ were taken from McCoy and Smith (Jour. Am. Chem. Soc., vol. 33, 1911, p. 466). The data for calcium carbonate were included in the table to show the effect

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of carbon dioxide on its solubility, inasmuch as $CaCO_3$ is always present in the reaction. Variation of the pressure of CO_2 above 1 atmosphere does not seriously affect the ratio of the solubilities of $MgCO_3$ and $CaCO_3$, but the continuous decrease in the ratios indicates that carbonation at high pressures will yield a slightly less pure product than at lower pressures.

From the above table, it will be noted that the greatest rate of change of solubility with respect to partial pressure of the CO_2 occurs between 0 and 1 atmosphere partial pressure. On this basis it would seem possible to operate the carbonation process efficiently at atmospheric pressure and thereby obviate the necessity of burdening the process with the cost of an expensive compressor. This has been suggested by Henton.

Osokoreva (36) points out the danger of overcarbonation of the milk of dolomitic lime. He found that the solubility of the $Mg(HCO_3)_2$, which is marked during the early stages of carbonation, decreased after extended carbonation with the precipitation of basic magnesium carbonate. Henton (35) noted supersaturation of the $Mg(HCO_3)_2$ solution, which might possibly account for the observations of Osokoreva. Another possible cause for this precipitation may be the dehydration of the magnesium ion. Freshly precipitated magnesium carbonate contains three molecules of water and is several times as soluble as anhydrous magnesium carbonate. It is possible that the water of hydration of this material may be bound to the magnesium ion rather than to the carbonate ion. This water of hydration increases the solubility product of the corresponding hydrated magnesium carbonate. In the subsequent treatment of the suspension with carbon dioxide this permits an even greater solubility of the hydrated magnesium carbonate than was shown in the preceding table, and thereby also permits a greater $MgCO_3 : CaCO_3$ ratio. Unfortunately, the hydrated form of $MgCO_3$ is not the stable form, and dehydration proceeds slowly. When an appreciable degree of dehydration has been attained, the anhydrous or possibly the basic carbonate is precipitated to produce the effect noted. The relationship between solubility of $MgCO_3$ in a solution saturated with CO_2 at about 1 atmosphere pressure and the temperature of the solution is shown in the table below.

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Relation of temperature to solubility of $MgCO_3$ in a saturated CO_2 solution

Temp. ° C.	$MgCO_3$/ liter, gm.	Temp. ° C.	$MgCO_3$/ liter, gm.
13.4	28.45	70	8.1
19.5	25.79	82	4.9
29.3	21.95	91	2.4
46	15.7	100	.0
62	10.4		

Note. - The data for this table were taken from Engel and Ville, loc. cit.)

As the temperature rises, the solubility of the $MgCO_3$ or $Mg(HCO_3)_2$ falls continuously, until at 100° C. its solubility is nil. During the rise in temperature the CO_2 is liberated from solution as a relatively pure but wet gas. The magnesium carbonate can often be liberated without boiling the solution, but the colloidal nature of the precipitate formed below the boiling point necessitates a slight boiling period to facilitate handling. The length of the boiling period is of considerable importance, inasmuch as it affects the properties of the properties of the product and its chemical composition. The longer the period of boiling, the more basic the precipitate.

It will be noted from the table above that a solution at room temperature saturated with $MgCO_3$ and CO_2 at one atmosphere pressure contains less than 2.8 percent $MgCO_3$. This means that for each pound of MgO produced, at least 75 pounds of water must be pumped, heated, and handled, requiring huge apparatus. This process, therefore, can be used for the manufacture of only comparatively high-cost products that can bear the equipment expense. On the other hand, the only raw materials needed are dolomite and coke or coal with a little water for make up, and the process may therefore be located without consideration of other raw materials or reagents. It seems possible, moreover, that with efficient design, including enough apparatus for heat exchange and recovery, no external source of heat would be needed other than from the dolomite kiln. Thus, in a continuous process, the hot water remaining after precipitation of basic magnesium carbonate could be treated with calcined dolomite to yield milk of lime and produce enough heat of reaction to provide steam for boiling the basic magnesium carbonate slurry. The hot milk of dolomitic lime would then pass through a heat exchanger to preheat $Mg(HCO_3)_2$ solution for precipitation of basic carbonate. The milk of dolomitic lime itself would thereby be cooled for reaction with CO_2 although it might be necessary to add an auxiliary cooler to reduce the temperature further to the desired level. The heat exchanger involved may become scaled with precipitated magnesium carbonates and cause

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difficulty. However, modern equipment and the use of suitable surface active agents should largely prevent this scaling and permit satisfactory operation.

Kippenberger and others (37) based a process for the decalcification of dolomite on the fact that $MgCO_3$ forms soluble double salts with alkali bicarbonates. In his process, a filtered precipitate containing $MgCO_3$ is agitated with a strong solution of alkali bicarbonate. The resulting solution is filtered after a lapse of about 20 minutes, and the filtrate is set aside to crystallize. Crystallization begins 1 to 2 hours after initial solution and ends after about 18 hours. $MgCO_3 . 3H_2O$ is formed above 15°C., and $MgCO_3 .. 5H_2O$ below that temperature. The alkali bicarbonate recovered after crystallization of the hydrous magnesium carbonate may be used repeatedly.

Kiepenheuer (38) modified Kippenberger's process by treating calcined dolomite with CO_2 under pressure in a Na_2CO_3 solution, thereby forming $MgCO_3$ and $NaHCO_3$ almost simultaneously and in a very reactive state. The magnesium carbonate rapidly goes into solution and is later precipitated from the filtered fluid when the pressure of CO_2 is reduced. Platzmann (39) dissolves $Mg(OH)_2$ in water containing $KHCO_3$ by treating the suspension with CO_2 to form the somewhat soluble $MgCO_3 . KHCO_3 . XH_2O$. The magnesium carbonate (hydrated with three molecules of water) is recovered from this solution by heating to 100° C. A total of about the equivalent of 1 percent of MgO may be dissolved in the solution. These processes appear to have but a slight advantage over the Pattinson process and must bear the additional cost of a make-up reagent.

6. Processes Involving Soluble Magnesium Salts.

Precipitation of Magnesium Hydroxide. - Perhaps the most obvious chemical method for obtaining magnesia is to precipitate it as $Mg(OH)_2$ from a solution containing a soluble magnesium salt by adding a more soluble strong hydroxide. The bulk of the magnesia sold commands comparatively low prices, and therefore the cheapest hydroxide consistent with the quality of the magnesia product desired should be used. Calcium hydroxide, the cheapest alkali available, is used in the precipitation of refractory and other bulk grades of magnesia. The yield of magnesia is doubled if dolomite is used as the source of the calcium hydroxide. The magnesia in the dolomite does not take part in the reaction but unites with the precipitated magnesium hydroxide to increase the yield of magnesia.

If magnesium hydroxide is precipitated rapidly from solution without suitable precautions, it will consist of a colloidal gelatinous mass very difficult to handle. Much study has been devoted to overcoming this obstacle to successful recovery of magnesium hydroxide, and various methods devised for coping with the problem are discussed in following paragraphs.

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The methods by which precipitated magnesium hydroxide is rendered readily filterable may be divided into two classes - (1) those that cause the precipitation of a coarsely granular material and (2) those that cause the formation of a highly flocculant or aggregated mass that is readily filterable.

The precipitation of a granular magnesium hydroxide depends on the slow formation of the precipitate and is perhaps accomplished most readily by the addition of lime in such a manner that it rapidly becomes coated with a gelatinous film of $Mg(OH)_2$, which impedes the progress of the reaction and thereby allows the formation of granular $Mg(OH)_2$. In one process slaked lime in the form of a thin paste is added to the solution of magnesium chloride in fine streams, which become long threads coated with $Mg(OH)_2$. After about 6 days these threads are converted into solid $Mg(OH)_2$ by diffusion of the reactants through the outer skin. The product is then ground, washed, dried, and possibly calcined.

Chesny (40) suggests that a slurry of calcined dolomite slaked in concentrated suspension so as to produce relatively coarse crystals of $Ca(OH)_2$ be added to the magnesium-containing solution at a rate that will insure effective mixing but prevent or restrain the production of colloidal hydrates of $Mg(OH)_2$. The method described consists in establishing flow streams of the magnesium-containing brine and unclarified milk of lime or milk of dolomitic lime. These streams are brought together in a reaction chamber and agitated just enough to cause slow reaction. The quantity of milk of lime added is restricted to that necessary for reaction with not more than 90 percent of the original magnesium in the brine. The slow reaction of relatively coarse crystals of $Ca(OH)_2$ in an excess of magnesium in solution causes the formation of a precipitate of coarse (5 to 25 microns) crystals of $Mg(OH)_2$, which are substantially free of colloidal hydrates and are readily settled, filtered, and washed.

Farnsworth and Martin (41) suggest a similar process in which the lime is added as a solid of fine particle size. $Mg(OH)_2$ formed on the surfaces of the particles acts as a permeable membrane that restricts the rate at which the lime passes into the liquid phase, which in turn reduces the rate of reaction between the lime and the brine and causes the formation of a granular $Mg(OH)_2$. The lime is held in suspension by suitable agitation until the reaction has been completed.

In an earlier patent, Farnsworth and Montgomery (42) suggested the formation of coated particles of calcium hydroxide as a separate operation. Milk of dolomitic lime was given a preliminary treatment with part of the magnesium solution to be used to yield a diluted milk containing particles of calcium hydroxide coated with magnesium hydroxide. Such particles reacted slowly and yielded a crystalline $Mg(OH)_2$ product.

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Mastin (43) obtained a satisfactory precipitated $Mg(OH)_2$ by gradually mixing, with a charge of granulated quicklime, enough bittern-carrying water for substantially complete slaking of the lime and a magnesium salt (usually the chloride) equivalent to about a quarter of the total amount of bittern. The magnesium salt reacts with the lime to form some magnesia. The rate of mixing the bittern with the lime or calcined dolomite should be such as to maintain the mixture as a hot, plastic, steaming mass. The mixture is agitated until the lime is almost completely hydrated, and then more bittern is gradually added to the plastic mix to react with the remaining $Ca(OH)_2$ yielding $Mg(OH)_2$ in the form of a thin slurry. The $Mg(OH)_2$ so formed is a spongy, hydrated mass readily recoverable by filtration.

Wienert (44) suggests slaking the calcined dolomite with a solution containing an alkali or alkaline-earth nitrate, an alkali chlorate or calcium chloride, and a minor proportion of boric acid or alkali borate previous to its treatment with the $MgCl_2$ solution to produce easily filterable magnesia. Likewise, Lee and Lee (45) suggest calcining the dolomite in the presence of about 2 percent of a compound containing boron or beryllium, such as colemanite, razorite, borax, boric acid, beryllium oxide, beryl, or phenacite, and treating it with an $MgCl_2$ solution containing $CaCl_2$ to yield a readily filterable crystalline $Mg(OH)_2$. According to another method (46), an easily filterable $Mg(OH)_2$ is produced by carrying out the precipitation in a solution containing large quantities of alkaline earth nitrates or chlorides, particularly $CaCl_2$.

Chesny (47) treated a magnesium-bearing brine with a dilute pure milk of lime with slight agitation and obtained flocs of gelatinous $Mg(OH)_2$, which settled rapidly without breaking into finer particles. This type of $Mg(OH)_2$ is considerably more reactive than the more coarsely crystalline type and is preferred for certain purposes. Such material may be washed by redispersing the settled flocs to a suitable size at the top of a tall tower and allowing them to settle through a rising stream of clear water. The soluble impurities are removed by diffusion from the flocs into the wash water.

Various other methods and apparatus have been developed to facilitate washing of the gelatinous type of $Mg(OH)_2$. Soluble impurities may be removed from $Mg(OH)_2$ that has been precipitated in a gelatinous form by first drying the material to remove adsorbed water and then washing the resulting granular material with water to dissolve the remaining soluble salts (48).

Shikin and Spiro (49) suggest precipitation of $Mg(OH)_2$ in the presence of tanning extract to accelerate the settling, filtration, and washing of $Mg(OH)_2$. Another process (50) yields a granular product by precipitating the $Mg(OH)_2$ in the presence of a colloidal condensation product of an aldehyde and phenol or urea. Sisson (51) dissolved a concentrated slurry of the colloidal precipitate with CO_2 and then precipitated a satisfactory basic magnesium carbonate by heating the solution.

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Some Natural Magnesium-containing Solutions. - Sources of solutions of magnesium salts are numerous, and $Mg(OH)_2$ may be precipitated economically from many of them by using calcined dolomite. Perhaps the earliest large-scale sources of magnesium salt solutions to be utilized in producing commercial magnesia were the bitterns that remained at salt works after the bulk of the salt had been extracted from sea water. The solids content of these bitterns has a range of compositions as follows:

	Percent
NaCl	6 - 60
KCl	5 - 10
$MgCl_2$	20 - 60
$CaSO_4$	0.5 - 2.0
$MgSO_4$	10 - 25
$MgBr_2$	0.6 - 1.0

Approximately 25,000 tons of magnesium is contained in the salts of domestic sea-water bitterns produced annully. This would be equivalent to somewhat over 40,000 tons of MgO potentially available annually if precipitated without the use of dolomite, or double this amount if dolomite were used. Unfortunately, dolomite is not readily available near the bitterns, and precipitation is generally accomplished with the aid of oystershell lime.

Another rather abundant source of solutions of magnesium salts is the magnesium-containing natural brines such as are found in Michigan and in the Ohio Valley. These brines are somewhat more favorably situated with respect to dolomite for precipitation purposes and also to the markets for magnesia and magnesia products than are the sea-water bitterns. Several plants are now producing or will shortly produce magnesia products by precipitating the magnesia from these natural brines by the use of dolomite. A typical analysis of the solids content of these brines follows:

	Percent
Cl	61.6
Na	31.5
Ca	4.9
Mg	1.3
Other	.7

The solids content of these brines ranges from 10 to about 30 percent. Concentration of the magnesium in these brines is considerably less than that in sea-water bitterns, and therefore more difficulty would be experienced in recovering the magnesia directly from the brines. However, after extraction of the salt, the concentration of magnesium is greater in the remaining bitterns, and they may be utilized economically. Such bitterns usually

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consist of a mixture of calcium and magnesium chlorides, with the former in excess. Plants using both bitterns and natural brines are now in operation.

The ocean is the largest source of naturally occurring magnesium-containing solution. This source, although virtually inexhaustible, is a very dilute source of magnesium; only 0.14 percent of its weight is magnesium ion. However, natural brines used as sources of magnesium are quite dilute. Unconcentrated ocean water has for some years been used as a source of magnesium compounds, and the quantity of magnesium being extracted from the ocean is increasing rapidly. Until recently, these operations were not carried on at locations near sources of dolomite, and oystershell lime was therefore used as a precipitant of the magnesium-ion content. In 1942 a plant was built at Cape May, N. J., to recover from sea water 35,000 tons of magnesia annually for refractory purposes. Precipitation is accomplished with the aid of dolomite obtained from eastern Pennsylvania.

From the preceding dicussion it is evident that precipitation of magnesium from concentrated solutions should present little difficulty, because various solutes (especially calcium chloride, the salt formed by the reaction of $Ca(OH)_2$ and $MgCl_2$) in the solutions act as floculating agents. However, the process becomes much more difficult with dilute solutions, such as sea water, because special precautions are necessary to prevent the formation of a colloidal gelatinous precipitate, which is difficult to settle and filter, and also because of the great volume of water from which the $Mg(OH)_2$ is removed. The difficulties of processing dilute solutions for the recovery of magnesia have been overcome successfully, and economical large-scale recovery of the magnesium content has been accomplished in many plants, both in the United States and in Europe.

Cyclic Processes. - $Mg(OH)_2$ may also be recovered from dolomite by use of magnesium-containing solutions other than those occurring naturally. Several cyclic processes involving the use of magnesium chloride have been devised, and numerous modifications have been suggested for use in localities far from the sea or from natural brines.

One of the simplest and most direct of the cyclic processes is that proposed by Closson and modified by Robinson and others (52). In this process a solution of magnesium chloride is treated with a purified milk of dolomitic lime to produce magnesium hydroxide and a corresponding solution of calcium chloride. The lime content of the dolomite is removed most efficiently by using somewhat less than the stoichiometric quantity of milk of dolomitic lime. The $Mg(OH)_2$ is filtered, washed, and calcined to produce a product claimed to contain 97 percent MgO with only 2 percent CaO and 1 percent Fe_2O_3. The calcium chloride solution is treated with more milk of dolomitic lime and CO_2 in a type of gas scrubber, resulting in the formation of $CaCO_3$ and more of the $MgCl_2$ solution. The $CaCO_3$ is removed from the solution, and the $MgCl_2$ is used again in the process. About 6

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percent of $MgCl_2$ is lost during each cycle, but this will vary somewhat with the efficiency of the operation. Economy of operation demands a cheap and convenient source of $MgCl_2$ or $CaCl_2$. Fortunately, the Solvay process for the production of sodium carbonate yields somewhat over 3,000,000 tons of calcium chloride annually and, as almost 95 percent of it is wasted because of lack of market, this byproduct should constitute a low-priced source of reagent for use in the precipitation of magnesia.

The quantity of impurities in the product obtained from the above-described cyclic process should be about half that from the simple leaching of lime from the dolomite either by water alone or by various solutions, because twice as much magnesia is obtained per unit of impurities present.

The above process may be modified to facilitate the recovery of magnesia by calcining the dolomite in the presence of $MgCl_2$ (either dry powder or solution) at low temperatures. The reaction starts as low as 150° C. with some materials and is completed for all materials at temperatures below 750° C. CO_2 is evolved, and the MgO and $CaCl_2$ formed by the reaction are easily separated by leaching out the very soluble $CaCl_2$ (53). The cyclic process may be continued from this point as in the method of Robinson. That this modification may operate satisfactorily, however, either the dolomite must be in a form fine enough to absorb the requisite quantity of $MgCl_2$ solution before calcining, or solid $MgCl_2$ must be used. Fineness facilitates reaction; therefore, at least a grinding and leaching operation are added to the process whereas only a precipitation operation is omitted.

This process is most advantageous for dolomite of high purity because it is not adapted to elimination of impurities.

Other methods to facilitate the collection of the MgO have been devised. It is claimed (54) that the presence of ammonia or an ammonium salt in solution aids the precipitation of magnesium hydroxide, probably by increasing the solubility of the $Mg(OH)_2$ and thereby facilitating the formation of relatively coarse crystals.

MacIntire (55) employs ammonia for a different purpose. In his process, the magnesium chloride solution is treated with a slight excess of slaked dolomite, producing a relatively pure $CaCl_2$ solution and a magnesium hydroxide containing some calcium hydroxide. The $CaCl_2$ solution is then treated with ammonia and CO_2 to precipitate a pure $CaCO_3$ and yield an ammonium chloride solution. It is then treated with impure $Mg(OH)_2$, which reacts only with difficulty, releasing ammonia from solution on boiling. This treatment yields an impure $MgCl_2$ solution that may be re-used in the process ammonia that is collected and re-used, and $Mg(OH)_2$, which is free of $Ca(OH)_2$. This process, which involves a rather complicated operation and the use of

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an expensive reagent, produces a high-grade calcium carbonate and a good grade magnesia and therefore may be of some commercial interest.

The Robinson process may also be modified by using either finely ground raw dolomite or half-burned dolomite in the second part of the process in which $MgCl_2$ is regenerated from $CaCl_2$. The use of finely divided raw dolomite, as in the magnesium bicarbonate process, would greatly reduce the rate of reaction and probably would not be economical. The use of a half-burned dolomite might be somewhat advantageous in that it would reduce the calcining temperature and would correspondingly reduce the quantity of CO_2 required for the reaction.

Clerc and Nihoul (9) suggest the cyclic process involving $MgCl_2$ as a means of improving the quality of the product obtained by mechanical separation of lime and magnesia from dolomite. The capacity of a given apparatus could be increased by use of a previously concentrated magnesia. The reagent losses, however, are about proportional to the $Mg(OH)_2$ produced and represent largely material that cannot be economically recovered from the filtered solids. These losses, therefore, would be only moderately reduced by the handling of a smaller quantity of $CaCO_3$. Consequently, it is doubtful whether the cost of the extra beneficiation operation would be justified. The saving, however, would be much more appreciable in the processes involving larger volumes, as in the direct water-solution method previously described. In these processes the reagent loss and cost is much less important (water is usually very cheap), and the reduced size of apparatus necessary would represent an appreciable saving. As previously brought out, however, most mechanical beneficiciation methods are applicable only to magnesitic limestones containing the magnesite and calcite as discrete particles.

Dougherty (56) suggests a novel process involving treatment of calcined dolomite with a solution of $MgCl_2$ to yield $Mg(OH)_2$ and $CaCl_2$ in solution. The latter is then treated with $MgSO_4$ obtained by dissolving dolomite in sulfuric acid. The reaction regenerates $MgCl_2$ for re-use and precipitates calcium sulfate. The products of these reactions are a relatively pure calcium sulfate and a satisfactory grade of magnesia. The reactions involved may be summarized as follows:

$$MgCO_3 \cdot CaCO_3 + 2H_2SO_4 \rightarrow MgSO_4 + CaSO_4 \cdot 2H_2O + 2CO_2$$
$$CaSO_4 \cdot 2H_2O + MgSO_4 + CaCl_2 + 2H_2O \rightarrow 2CaSO_4 \cdot 2H_2O + MgCl_2$$
$$MgCl_2 + Mg(OH)_2 + Ca(OH)_2 \rightarrow 2Mg(OH)_2 + CaCl_2$$

The net reaction of the process is :

$$MgCO_3 \cdot CaCO_3 + Mg(OH)_2 + Ca(OH)_2 + 2H_2SO_4 + 2H_2O \rightarrow 2Mg(OH)_2 + 2CaSO_4 \cdot 2H_2O + 2CO_2$$

The economic success of such a process is doubtful.

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Schulze (57) suggests a process for the production of anhydrous neutral magnesium carbonate that involves treatment of dolomite with a solution of magnesium chloride and carbon dioxide. The reaction is carried out at about 150° C. and at sufficient pressure to maintain this temperature. The $MgCl_2$ solution is regenerated by treatment with calcined dolomite and CO_2 as previously described. This process is designed to obtain special products rather than to maintain low costs.

Calcination of Magnesium Chloride Obtained from Dolomite and Calcium Chloride. - Another method of recovering magnesia from dolomite that might be of interest involves the use of the calcium chloride solution obtained as a byproduct from the Solvay process of making sodium carbonate. The calcium chloride solution is treated with calcined dolomite and carbon dioxide to produce calcium carbonate and a solution of magnesium chloride. The calcium carbonate is removed by settling, and the magnesium chloride solution is treated with lightly calcined magnesia in an amount equal to about one-third the dry weight of the magnesium chloride in the solution. This causes the formation of a magnesium oxychloride, which precipitates from solution and is readily recoverable by filtration or centrifuging. The oxychloride is then heated at 600° to 700° C. in the presence of water vapor, and the magnesium chloride therein decomposes according to the following equation:

$$MgCl_2 + H_2O \rightarrow MgO + 2HCl$$

To prevent oxidation of HCl to Cl_2, all free oxygen must be excluded from the reaction area. The HCl is recovered by adsorption in water. All the operations of this process are described in the literature (58).

This process is of interest for several reasons. First, it provides an outlet for the calcium chloride solution obtained as a waste byproduct in the Solvay process and which often presents a serious disposal problem; second, calcium chloride is a very low-cost raw material and is abundant; third, a valuable byproduct, hydrochloric acid, is produced and can help in sharing the cost of an already fairly economical process. Almost 2 pounds of hydrochloric acid is produced for every pound of magnesia obtained by this reaction, and its cost would be low enough to encourage its substitution for sulfuric acid in many local applications. Even more important is the possibility of oxidizing it to chlorine.

Inasmuch as the magnesia produced by this process is obtained from a precipitated product, it should be of high purity. Small quantities of chloride may be removed either by leaching or by calcining at a high temperature. For many uses the traces of chloride may not be objectionable.

A problem of considerable importance is disposal of the calcium carbonate, which is produced as a byproduct five times as great in quantity

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as the magnesia. Part of it could be calcined to lime and re-used in the Solvay process, and part might be marketed as fertilizer, whiting, or for chemical use.

7. Processes Involving Use of Ammonia or Ammonium Salts.

Several processes have been devised for the separation of magnesia from dolomite that involve the use of ammonia or ammonium compounds. The most direct and simple of these depends upon the solubility of calcium hydroxide in solutions of ammonium salts. For instance, $Ca(OH)_2$ added to an NH_4Cl solution of a concentration usually not exceeding 15 percent replaces the ammonia, leaving it in solution as NH_4OH, and the calcium chloride formed also goes into solution. Magnesia and magnesium hydroxide are much less soluble than $Ca(OH)_2$; therefore, the lime may be leached from calcined dolomite by using a solution of ammonium salts, and a fairly good grade of magnesia may be prepared from the residue. The ammonium solution is recovered by passing CO_2 into the solution, thereby precipitating the calcium as carbonate and regenerating the ammonium chloride solution for re-use. This process has been described by Barrett (58). It is both simple and direct but uses a relatively high-cost reagent, NH_4Cl, any losses of which would weigh heavily against the process.

Many modifications of this process have been suggested, but the most important is that which adapts it to employment in the Solvay process. One procedure suggested (9, 60) is that milk of dolomitic lime be substituted for milk of high-calcium lime in the Solvay process. If the milk of high-calcium lime ordinarily used in this process is replaced by an equal molar quantity of milk of dolomitic lime, the resulting solution will contain both calcium and magnesium chlorides and must be treated with more calcined dolomite to precipitate the magnesia. This process is somewhat unsatisfactory, as it is difficult to drive ammonia from ammonium chloride solution with magnesium hydroxide. Moreover, it involves a second operation, namely, the precipitation of magnesia from the mixed chlorides solution. Both of these difficulties may be overcome by increasing the milk of dolomitic lime to double the equivalent of high-calcium lime ordinarily used. If that quantity is used, the calcium hydroxide only will be consumed in the liberation of the ammonia, and the sludge of magnesia remaining may be separated from the calcium chloride solution, washed, and calcined to produce the desired magnesia product.

Current developments seem to indicate that the latter procedure may become one of the simplest and most important methods of recovering magnesia products from dolomitic raw materials. The process should fit smoothly into the existing Solvay process and would require only minor changes in design of the plant to accommodate milk of dolomitic lime instead of milk of high-calcium lime. The additional apparatus would consist merely of

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standard settling, filtering, possibly mixing, calcining, and packaging equipment. The volume of possible production by this mehtcd is enormous. Based on 1940 figures for the production of sodium carbonate by the Solvay process, the potential production of magnesia by this method is 1,700,000 tons annually.

In this process, however, as in other processes previously described in which the lime content is dissolved tc leave a sludge of magnesia, the dolomite used must be of high purity and carefully calcined, and the milk of dolomitic lime must be clarified to insure a reasonably pure product.

To remove objectionable impurities, Blumenfeld (61) suggests dissolving the magnesia with HCl of such concentration that the silicates, aluminates, iron, and other impurities will remain as a residue. Kippe (62) recommends partial precipitation of the resulting $MgCl_2$ solution with NH_3 to yield a very pure magnesia, and precipitation of the remaining $MgCl_2$ with purified milk of dolomitic lime to yield a magnesia suitable for refractory purposes. By adding enough calcined dolomite in the second precipitation, the ammonia in the solution may be liberated and recovered by boiling. The complicated process and comparatively high cost of HCl however, are serious drawbacks to these suggestions.

The Kippe method may be changed into a cyclic process whereby a magnesium chloride solution resulting from the treatment of calcium chloride with calcined dolomite and CO_2 is treated with ammonia to precipitate a pure $Mg(OH)_2$. After removal of the $Mg(OH)_2$, the solution is treated with enough calcined dolomite to precipitate all of the $MgCl_2$ and to liberate all the ammonia, which is removed from the solution by boiling. A calcium chloride solution results from this operation, and an impure $Mg(OH)_2$ is obtained. The $CaCl_2$ solution is again treated with calcined dolomite and carbon dioxide to precipitate calcium carbonate and regenerate an $MgCl_2$ solution, which is returned to the cycle, and the ammonia expelled is also returned to the cycle to precipitate more of the pure $Mg(OH)_2$. By this cyclic process much of the magnesia is obtained in a higher state of purity and with a greater range of usefulness than would otherwise be possible. The method is somewhat similar to the cyclic chloride process of Robinson (52), which has previously been described but which is more costly. However, the additional cost may be compensated by the increased selling price of the purer product.

Rodolfo (63) suggested that half-burned dolomite be autoclaved at 110° C. with $(NH_4)_2SO_4$ to produce $MgSO_4$ and liberate ammonia. The insoluble calcium carbonate and siliceous material is filtered from the solution of magnesium sulfate, and the solution is then treated with the liberated ammonia at a temperature below 40° C. to form magnesium hydroxide and regenerate ammonium sulfate for re-use. The process would undoubtedly produce a very

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pure magnesia, but whether satisfactory precipitation of $Mg(OH)_2$ by the ammonia alone would be possible is somewhat questionable. Addition of CO_2, however, would assure complete precipitation of the magnesium content of the solution as magnesium carbonate.

Barrett (64) suggested heating dolomite with ammonium chloride to form MgO and calcium chloride. Ammonium carbonate is given off during the calcining operation. Calcium chloride leached with water and added to the ammonium carbonate precipitates as calcium carbonate and leaves ammonium chloride in solution for re-use. This process avoids difficulties in the filtration of gelatinous magnesium hydroxide.

Curlewis (65) and Orlandi (66) suggest heating a material containing a magnesium carbonate with ammonium sulfate to the temperature of decomposition of the latter, at which point magnesium sulfate and a sublimate of ammonium carbonate will be formed. If dolomite is used, both magnesium sulfate and calcium sulfate will be formed. The magnesium sulfate is leached out, and the two sulfates are then treated separately with the ammonium carbonate obtained from the original heating operation, yielding precipates of magnesium carbonate and calcium carbonate, respectively, and solutions of ammonium sulfate that may be recovered for re-use. The magnesium carbonate thus obtained is very pure and may be substituted for that obtained by the Pattinson process. This pure material probably would command a price high enough to absorb the high costs of cyclic reagents and of a complicated process.

8. Miscellaneous Byproduct Processes.

Almost all processes that involve the dissolution of dolomite in an acid to form a soluble calcium salt could potentially produce magnesia as a byproduct.

Byproduct in manufacture of calcium nitrate. - Twynam and others (67) suggest the production of magnesia as a byproduct in the manufacture of calcium nitrate, a fertilizer material that has been widely used, especially in Europe. Several methods are possible, and aside from the fact that in them nitric acid is used to dissolve the calcium, these methods resemble quite closely some of the methods for separating magnesia from dolomite that involve magnesium chloride.

Briefly, the variations include the following: 1. Dolomite is dissolved with nitric acid, and the clarified solution is treated with purified milk of dolomitic lime to precipitate magnesium hydroxide. 2. Milk of dolomitic lime is treated with nitric acid to yield calcium nitrate and magnesia. 3. Milk of dolomitic lime is formed in preparation for the following process:

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Part of the milk of dolomite is purified; the residue of coarse particles removed in the purification operation is added to the remainder of untreated milk of dolomitic lime and acted upon by nitric acid to yield the corresponding nitrates; the clarified nitrate solution is then treated with the purified milk of dolomitic lime to precipitate magnesia and yield a solution of calcium nitrate; the calcium nitrate in solution is evaporated, dried and marketed as fertilizer, and the precipitated magnesia is treated in the usual manner to produce a marketable product. 4. Dolomite is dissolved in nitric acid, and magnesia is precipitated with an excess of ammonia. The ammonia may be recovered by addition of milk of dolomitic lime and boiling, or the excess may be neutralized with CO_2 evolved from the dissolution of dolomite in HNO_3 and a fertilizer material prepared from the reaction products.

Some work has been done on nitric acid cyclic processes for the production of magnesia from dolomite (68), but recovery of the nitric acid has presented considerable difficulty. Upon application of heat, calcium nitrate decomposes into lime, oxygen, nitrogen, and oxides of nitrogen. If the heating operation is controlled carefully, the oxides of nitrogen rather than elementary nitrogen may be formed, and these oxides may readily be converted into nitric acid for re-use. Unfortunately, such control has not yet been attained, and therefore the cyclic process is not completely satisfactory. Moreover, the process involves the rather difficult operation of evaporating the calcium nitrate solution to dryness.

Several of the processes for obtaining magnesia from dolomite by the cyclic chloride process could technically be applicable to nitric acid and nitrate processes. It is very doubtful, however, that such cyclic processes would be commercially successful, owing to the relatively high cost of nitrates.

Byproduct in manufacture of calcium acetate. - A small quantity of magnesia may be obtained as a byproduct in the manufacture of calcium acetate from pyroligeous liquors, and a process has long been suggested for this purpose (69). In this process, purified milk of dolomitic lime is treated with the pyroligneous liquors of hardwood distillation, which consist largely of a dilute solution of acetic acid and some more complex organic acids and tarry materials. The pyroligneous acid is used in such quantity that only the lime is attacked; the magnesia is left as a residue and is recovered. The magnesia obtained in this process is 80 to 90 percent pure, depending on the quality of the dolomite used. The solution containing the dissolved calcium is either treated with sulfuric acid for the recovery of acetic acid and the simultaneous production of calcium sulfate or is evaporated to dryness and sold for the production of acetone.

Several thousand tons of magnesia is potentially recoverable from dolomite annually by this process. The individual operations are on a small scale, and the quality of the product is so low that its uses are limited and marketing is difficult.

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Byproduct in manufacture of calcium hypochlorite. - Another possible source of magnesia from dolomite is in the calcium hypochlorite industry. In the process suggested by Wygal (70), dolomite is calcined and the lime content slaked to form $Ca(OH)_2$, which is then chlorinated in the presence of water to form $Ca(OCl)Cl.H_2O$. The reaction is stopped when substantially all the calcium hydroxide but none of the magnesia has been chlorinated, and the magnesia is recovered by filtration. As the calcium hypochlorite industry is of very considerable magnitude, this process presents a rather important potential source of magnesia. For this process to become economically feasible, however, some means must be taken to inhibit the catalytic decomposition of the hypochlorite by the magnesia.

Byproduct in manufacture of synthetic formic acid. - A small quantity of magnesia may result from the production of synthetic formic acid or formates by a patented process (71) involving treatment of milk of dolomitic lime with carbon monoxide at 40 atmospheres pressure. The carbon monoxide reacts with the water and calcium hydroxide to form calcium formate; the magnesium hydroxide does not react but remains as a sludge, which may be recovered. The size of the formic acid industry, however, is so small that no great tonnages of magnesia could be produced.

Byproduct from pickling solutions and other solutions of heavy metals. - Processes that yield solutions of salts of heavy metals either as waste products or as sources from which the metal is to be recovered by precipitation as the oxide or hydroxide are potential sources of magnesia from dolomite (72). Both calcium hydroxide and magnesium hydroxide will displace most heavy metals from their salts. Therefore, milk of dolomitic lime may be added to the solution of heavy-metal salt; and the resulting solution of calcium and magnesium salts, after removal of the heavy-metal hydroxide or oxide, may be treated with more calcined dolomite to precipitate magnesia and yield calcium salt in solution. Exhausted pickling liquors are large sources of such solutions of heavy metals. However, if the liquors are sulfate solutions, the calcium will be precipitated with the metal hydroxide as the sulfates and the problem of separation becomes difficult. However, a relatively pure magnesium sulfate may be recovered from the solution.

9. Miscellaneous Processes.

Dow and Barstow (73) proposed a process for the production of magnesium chloride from dolomite. In their process, the chlorine released by the electrolysis of fused magnesium chloride in the manufacture of metallic magnesium is treated with SO_2 and water to form a mixture of hydrochloric and sulfuric acids. When a calcium chloride solution is added, it reacts with the H_2SO_4 to form calcium sulfate and more hydrochloric acid. The latter is used to dissolve dolomite with the formation of carbon dioxide and a mixture

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of calcium and magnesium chlorides in solution. The solution is boiled with milk of dolomitic lime to precipitate magnesium hydroxide, which is separated by filtration, leaving a calcium chloride solution to be used again in the process as above. The $Mg(OH)_2$ is treated with more HCl and yields an $MgCl_2$ solution, which is evaporated to dryness and used in the process of making magnesium metal.

The above process may be greatly simplified if powdered dolomite made into a slurry with water is treated with an equimolecular mixture of chlorine and sulfur dioxide, forming magnesium chloride in solution, calcium sulfate, and carbon dioxide. The magnesium chloride solution is purified by filtration and is evaporated to dryness for use in the electrolytic cell. In this process, the quantities of magnesia and lime in the dolomitic raw material must be balanced carefully so that no excess of either sulfate ions or calcium ions is left in solution with the magnesium chloride.

The second of the above processes may be employed successfully if the dolomite used is so high in magnesia that by blending it with lime or dolomitic material lower in magnesia it is possible to produce the desired equimolecular ratio of $MgCO_3$ to $CaCO_3$. However, the occurrence of such dolomite is not widespread, and possible application of the process is thereby limited. Moreover, the sulfur used in these processes, to the extent of 1 1/3 parts or more per part of magnesium metal produced, is a valuable raw material, and the only byproducts obtained to offset its cost are calcium sulfate, a relatively low-priced commodity, and carbon dioxide, which would doubtless be a waste product. These processes are of relatively minor importance compared with operations already described yielding cheap magnesium chloride from calcium chloride (a waste material) and dolomite (a low-cost mineral).

Delage (74) proposed to electrolyze a solution of $MgSO_4$ in a diaphragm cell and to neutralize the cell liquors with dolomite according to the following equation:

$$CaCO_3 \cdot MgCO_3 + MgSO_4 + 2H_2O \rightarrow 2Mg(OH)_2 + 2H_2 \text{ (all at the cathode)} + CaSO_4 \cdot 2H_2O + 2CO_2 + O_2 \text{ (all at the anode or from anode liquor).}$$

The $MgSO_4$ for the process was to be obtained from the reaction between dolomite and niter cake, which is a byproduct in the manufacture of nitric acid from sulfuric acid and sodium nitrate. This reaction would also yield $CaSO_4$ and Na_2SO_4 simultaneously. The presence of Na_2SO_4 in the electrolytic cell would result in the formation of NaOH, an additional product of the process. Ultimately, calcium sulfate would be the only sulfate remaining.

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The process could doubtless be made cyclic by obtaining $MgSO_4$ for this reaction by treatment of a suspension of finely divided $CaSO_4$ with milk of dolomitic lime and CO_2. The hydrogen and oxygen obtained as coproducts in Delage's process also have a market value. This electrolytic process might prove successful in areas having low-cost electric power.

Booth (75) patented a method of recovering magnesia from dolomite by dissolving it either in fused sodium or potassium chloride, or both, maintained at a temperature higher than the decomposition temperature of magnesite and lower than the decomposition temperature of the calcite. The $MgCO_3$ decomposes and forms a precipitate in the fused salt solution, and MgO is obtained from the suspension by hot filtration of the fused salt. The $CaCO_3$ is not decomposed but remains in solution in the fused salt, which is solidified and treated with water to dissolve the salt and leave a finely divided $CaCO_3$ residue. The salt solution is then evaporated for re-use. This process involves the use of an expensive solvent and includes several difficult and costly steps; therefore, its commercial success is doubtful.

Laurent and Baze (76) have patented two complicated processes by which magnesia may be obtained from dolomite. In the first, sodium chloride is heated with Al_2O_3 in the presence of steam to yield hydrogen chloride and sodium aluminate. The HCl reacts with dolomite, yielding a solution of magnesium and calcium chlorides. The liberated CO_2 is used to decompose the sodium aluminate into Na_2CO_3 and Al_2O_3. The latter is available for another cycle. The $CaCl_2$ in the solution obtained in the reaction of HCl on dolomite is treated with sodium sulfate to yield calcium sulfate and sodium chloride. The calcium sulfate is removed by filtration and treated with the Na_2CO_3 solution to yield Na_2SO_4 and CaC03. The Na_2SO_4 is returned to the process, and the $CaCO_3$ is either marketed or wasted. The solution remaining after the removal of calcium sulfate contains sodium and magnesium chlorides and is treated with sodium carbonate to yield magnesium carbonate and a solution containing only sodium chloride. (The calcium and magnesium contents of the chloride solution could, no doubt, have been separated equally well by fractional carbonation with sodium carbonate and without the intermediate use of sodium sulfate.) The sodium chloride solution is evaporated, and the salt returned to the process. The magnesium carbonate is calcined to produce the desired magnesia product. The net reaction of the whole process is

$$MgCO_3.CaCO_3 \dashrightarrow MgO+CO_2+CaCO_3$$

It will be noted that dolomite is the only raw material required for this process other than replacements of minor amounts of materials lost. This process is entirely too complicated to be of value in the recovery of magnesia from dolomite.

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The process may be modified in several ways. The mixture of sodium and magnesium chlorides may be separated by fractional crystallization rather than by chemical precipitation. This would yield an equivalent quantity of $MgCl_2$ and would also yield Na_2CO_3. The net reaction would be as follows:

$$2NaCl + MgCO_3.CaCO_3 \rightarrow MgCl_2 + Na_2CO_3 + CaCO_3$$

Another alternative to the process would be to employ purchased Na_2SO_4 for the precipitation of the calcium chloride and permit the formation of calcium sulfate as a byproduct. This would simplify the process somewhat, and the combined value of sodium carbonate and calcium sulfate is about equal to the combined value of sodium sulfate and calcium carbonate involved in the reactions. The net reactions with this modification, as applied to the previous two modifications, are as follows:

$$MgCO_3.CaCO_3+2H_2O+Na_2SO_4 \rightarrow MgO+Na_2CO_3+CO_2+CaSO_4.2H_2O$$
and
$$2NaCl+MgCO_3.CaCO_3+Na_2SO_4+2H_2O \rightarrow MgCl_2+2Na_2CO_3+CaSO_4.2H_2O$$

The Laurent and Baze process just described and the modifications suggested are so complicated that chance of their commercial success appears slight at least in the manufacture of refractory magnesia. It is possible, however, that they might be applied to the production of higher-priced products, such as basic magnesium carbonate.

According to another method suggested by Laurent and Baze (77), calcium sulfate is reduced with coal to calcium sulfide, which is treated in aqueous suspension with CO_2 to yield H_2S and $CaCO_3$. The H_2S is passed into a solution of $CaSO_4$ to yield H_2SO_4 and CaS. The CaS is separated by filtration and roasted to yield more $CaSO_4$. The H_2SO_4 is used to decompose dolomite into CO_2, $CaSO_4.2H_2O$, and $MgSO_4$. The $CaSO_4.2H_2O$ is separated by filtration for re-use, and the $MgSO_4$ is treated with Na_2CO_3 to yield $MgCO_3$ and Na_2SO_4. The $MgCO_3$ is separated from the solution and calcined to produce the desired magnesia product, and the Na_2SO_4 solution is evaporated to yield solid Na_2SO_4. Sodium carbonate may be regenerated from the Na_2SO_4 by the well-known although now obsolete Leblanc process, which yields not only the Na_2CO_3 but also H_2S for re-use.

The only raw materials involved in this process, other than to compensate for losses, are dolomite and carbonaceous fuel (usually coal). The only byproduct of the process as outlined above is calcium carbonate, which is obtained in a fairly pure state.

The method given above of recovering sulfuric acid from calcium sulfate is interesting but is more complicated and costly than existing processes. The

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dissolution of dolomite and the precipitation of calcium sulfate and magnesium carbonate are not unusual operations. The Leblanc process for the recovery of Na_2CO_3 from sodium sulfate is obsolete, having been replaced by more efficient means. Although in its application to the Laurent and Baze process, both the sodium carbonate and the hydrogen sulfide are used, the process is so complicated that it would probably be more economical to purchase the soda ash and hydrogen sulfide and market the sodium sulfate. It would probably be even more economical to purchase sulfuric acid direct rather than attempt to manufacture it by the process suggested. In view of these considerations, it seems difficult to justify this process economically.

Stull (13) suggested that just enough H_2SO_4 be added to milk of calcined dolomite to convert the calcium hydroxide into calcium sulfate, which forms in relatively large needle-shaped crystals. These crystals are then readily separated from the finer $Mg(OH)_2$ by a screening or other size-classification operation. A product containing 75 percent MgO has been obtained by this method. It is of little commercial interest, as the product obtained is of low MgO concentration, and an expensive raw material, sulfuric acid, is employed. It seems possible, however, that the method may be applied to recovery of magnesia from dolomite with the use of brines containing magnesium sulfate, which occasionally occur naturally; although it would doubtless be more efficient to remove the sulfate ions with calcium chloride obtained from a previous cycle before attempting to precipitate the magnesium content with calcined dolomite.

Lee (78) patented a process of adding to finely crushed dolomite a material such as iron oxide, which will react more readily with the lime than with the magnesia to form a fusible system, which may be removed from the magnesia. In an example, he suggests briquetting an intimate mixture of 10.8 parts of dolomite, 9 parts of brucite, and 4.8 parts of mill scale. Upon application of heat, calcium ferrites form, which drain from the briquettes, leaving a residue containing as much as 81 percent MgO. The relatively impure magnesia obtained by such a process is suitable for the manufacture of basic refractories. The calcium ferrite adhering to the magnesia is desirable as a flux for aiding in the sintering of the magnesia in furnace hearths. Magnesium orthosilicate (olivine) may be added to improve the refractory properties of the material by reacting with the fusible calcium ferrite to form less fusible calcium silicates.

GENERAL ECONOMIC CONSIDERATIONS

Cost of Production and Applicability of Process

Cost is the most important consideration in the recovery of any established commodity from a new source. The various grades of magnesia

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commercially available command a wide range of prices and therefore permit a wide range of manufacturing costs. The less pure items sold in great bulk at a low price must be manufactured on a large scale and at minimum expense. On the other hand, more highly refined or processed materials are sold in smaller quantities for higher prices and can afford more meticulous handling during manufacture.

Where raw materials are abundant, costs of manufactured commodities tend to decline as improvements are made in manufacturing practice. The raw materials for magnesia are exceedingly abundant, and therefore a continuous decrease in its cost of manufacture may be expected. Rather costly processes that can no longer be improved technically will doubtless be replaced gradually by more efficient processes. It is essential, therefore, that any contemplated process be studied carefully from this standpoint.

Processes must be so chosen that the product obtained will be suitable for the proposed use. Obviously, a process producing a low-grade product in great volume could not be employed to produce a high-purity product for which the market is small. Thus, the method of Mitchell (p. 7) for separating magnesia from dolomite by a differential hydration method would be entirely unsuited to the manufacture of milk of magnesia for medicinal purposes.

Magnesia for refractories.

The degree of purity desired in magnesias to be used for refractories varies greatly and depends on the type of refractory to be manufactured therefrom. At one end of the scale, a product having as little as 65 to 70 percent magnesia with 18 percent lime and 15 percent acidic oxides may be acceptable for grain refractories for open-hearth furnaces; whereas, at the other extreme, almost chemically pure magnesia may be required for fused magnesia refractories. The great bulk of the magnesia used for refractory purposes contains 80 to 95 percent MgO with up to 7 percent Fe_2O_3.

Magnesia to be used for the manufacture of refractory shapes, such as brick, should have very little residual porosity and should be of relatively high purity. Therefore, precipitated magnesias used in the manufacture of such refractory products must be calcined at temperatures as high as 1,870°C. (3,400° F.) to reduce their residual porosity before use. However, precipitated magnesias, owing to their great fineness, are readily adaptable to blending with other materials to yield products of closely controlled chemical composition and physical properties, and therefore satisfactory refractory materials have been produced therefrom.

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Magnesia for magnesium metal.

Magnesia for electrothermal reduction to magnesium metal should be relatively pure and in a finely divided state. Supplies of magnesia for this purpose must almost certainly be chemically prepared, as enough satisfactorily pure material from natural sources, such as calcined magnesite and brucite, is not readily available. The precision of chemical and physical control involved in some of the chemical processes for the production of magnesia described in this paper cannot be obtained in magnesias from natural sources.

Magnesia for reaction with either chlorine or hydrochloric acid for metal production by the electrolytic method should not only be pure but should also be fairly reactive to facilitate chlorination. However, it seems possible that there will be a trend in the future to use byproduct magnesium chloride, which may be abundantly available for the purpose and which will also yield the valuable byproduct, chlorine.

Magnesia for magnesium oxychloride cements.

Magnesia required for magnesium oxychloride cements must have not only the desired chemical composition but must also have carefully controlled physical properties. The presence of lime or calcium hydroxide in the magnesia is detrimental to the properties of the cement, and, therefore, the free-lime content is limited to less than 2 percent. The properties of the cement are dependent, also, upon the treatment of the material during calcining. The reaction yielding magnesium oxychloride should proceed at the optimum rate. Undercalcined magnesia is too reactive, whereas overcalcined material will be insufficiently reactive. The time and temperature of calcining must therefore be carefully controlled and varied according to the chemical composition and properties of the raw material. Inasmuch as the properties of any magnesia obtained mechanically or chemically from dolomite will be under close control, a satisfactory magnesia for cement purposes can be produced from dolomite more easily than by direct calcination of magnesite or brucite. However, careful control of the processing conditions has made possible the production of satisfactory plastic magnesia products from magnesite, and most of the magnesia for oxychloride cement has therefore originated from this source. The increasing production of magnesia from dolomite may soon alter this situation.

Chemical magnesia.

In general, chemical magnesias, whether for use as adsorbents, fertilizer or water conditioners, will depend on both purity and their physical properties, that is usually fineness of structure or particle size. Chemically precipitated magnesias are well suited to the manufacture of these products.

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Size and Location of Operation

The process best suited to a given magnesia product depends not only on the requirements as to cost of production and quality of the product, but also on the size and location of the operation.

In general, magnesia from dolomite for refractory purposes should be produced on a large scale at places fairly close to consuming areas. It would be futile to produce grain-refractory magnesia on a very small scale, because the necessary calcining equipment is expensive, and the competition in a large market from producers able to furnish substantial volumes at low cost would be great. Moreover, individual consumers often require quantities of magnesia comparable with or greater than those that could be produced by a small plant. Magnesias for fertilizers and for oxychloride cements should be marketed locally because of their bulk. The local market is often such that it will easily consume the relatively small quantities of these materials available from small byproduct operations. Magnesia for magnesium-metal production must be manufactured on a large scale because of the demands for huge quantities by individual consumers, and it must also be produced near the point of consumption to reduce charges for handling and transportation. Magnesia for pigment and chemical purposes requires close control and is therefore best produced in central plants, from which it can be shipped for greater distances than it would be profitable to ship cheaper magnesias.

A large plant may diversify its products; for instance, it may have small-scale refining equipment to produce specialties for which there is but moderate demand. Even the small plant may have a considerable degree of flexibility and may make a wide variety of products with only slight variation in its operation.

Economic Disposal of the Byproduct Calcium Compounds

A problem of major importance to all plants producing magnesia from dolomite is the disposal of the calcium compounds, $Ca(OH)_2$, CaO, $CaCO_3$, $CaCl_2$, or $CaSO_4 2H_2O$ obtained as byproducts. There is almost always a market for $Ca(OH)_2$ or CaO (hydrated lime or quicklime) of satisfactory purity and physical properties. However, the more usual form in which the calcium is obtained is as a sludge of calcium carbonate, the disposal of which has remained largely an unsolved problem because of the moisture content. Its fine state of subdivision and its low cost, however, suggest many interesting possibilities for commercial application. The sludge may be employed to advantage as a conditioner or fertilizer material in agricultural work, but the necessity of removing the water, combined with the low-cost $CaCO_3$, limits this application to the immediate vicinity of the producing plant, where the sludge itself may be transported economically. The sludge has been used in

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the manufacture of Portland cement in adjacent plants, and for this use it is particularly well suited owing to its fine particle size and its low magnesia content. In areas in which low magnesium limestone is not readily available the calcium carbonate sludge for use in Portland-cement manufacture may become a product of importance almost equal to that of the magnesia. A pure precipitated calcium carbonate residue could be dried and marketed as whiting, but it is doubtful if the present market for whiting could absorb the potential byproduct output of this material. However, it does not seem beyond the realm of possibility that the particles of the sludge could be so surface-treated or so precipitated as to produce, when dried, a very light, fluffy material that would have a low bulk density. Such material could doubtless be used as a filler, adsorbent, or low-temperature heat-insulating material. The sludge could be dried and calcined to high calcium lime, for which there is an active market. Uses for lime and uses that might apply to the calcium carbonate sludge or dried material are discussed at some length by Bowles and Jensen (78). A satisfactory solution to this problem of the economic disposal of the calcium carbonate byproduct would greatly increase the commercial attractiveness of several of the various processes discussed in this paper.

Calcium chloride is produced as a byproduct in several of the processes discussed. The economic disposal of this material is a problem upon which great effort has been expended over long periods of time and which still remains largely unsolved. About 95 percent of the calcium chloride produced as a byproduct of the Solvay process is still wasted. The use of calcium chloride in the production of magnesium chloride for magnesium metal and for magnesium oxychloride cements may present important future outlets for this commodity, and a process for the low-cost recovery of HCl from $CaCl_2$, possibly in conjunction with the manufacture of Portland cement, may be developed. The use of solid calcium chloride in dehumidifying and air-conditioning private homes and small, confined places where low humidity is necessary is of growing importance and may develop to considerable magnitude in the near future. Tyler (80) has discussed many of the uses to which calcium chloride is now put and which account for its present volume of sales. Although it appears as a byproduct in fewer of the processes for the separation of magnesia from dolomite than does calcium carbonate, nevertheless, the recovery of value from the $CaCl_2$ would be of material aid to the economics of the processes that do yield it as a byproduct. The solution of this problem would also be of great importance to the alkali industry.

In general, calcium sulfate should find markets comparable to the magnitude of its production, and no great problem should occur. Precipitated calcium sulfate may be used as a filler or pigment or may be calcined to yield a high-grade plaster. Other calcium compounds obtained are often equally as important as the magnesia and therefore have ready markets.

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CONCLUSIONS

In the foregoing discussion an attempt has been made to cover some of the various methods by which magnesia or magnesium compounds may be recovered from dolomite and to discuss their economic possibilities. It is hoped that a creative interest has been stimulated and that satisfactory attention has been directed to some of the possible methods of profitably recovering magnesia from dolomite.

The number and variety of economically sound methods discussed herein indicate that in the future all grades of magnesia can and will be produced from dolomite. It seems likely, therefore, that dolomite will become one of the more important sources of magnesia, and that, coincident thereto, future sources of magnesia products will be closer to consuming centers than heretofore.

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